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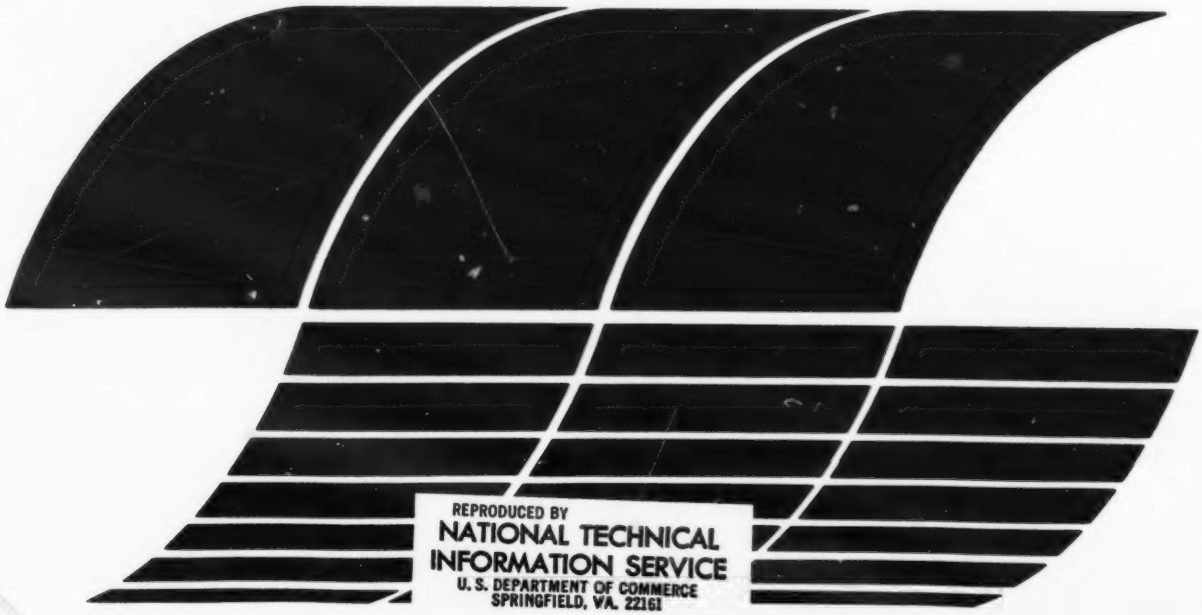

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ABSTRACT

The report gives results of a study to relate ground level NO2 concentrations to NOx emissions (NO2/NOx ratio) in plumes from six large power plants in the Chicago area, using a photostationary state reactive Gaussian plume model. The aim of the study was to assess the level of NOx control required to meet a probable short-term NO2 national ambient air quality standard (NAAQS). The major uncertainty of an earlier study (EPA-600/7-78-212) was its assumption of uniform, fixed NO2/NOx ratios of 0.5 (summer) and 0.25 (winter). The reactive model used in this study predicted significantly higher NO2/NOx ratios at the point of maximum plume impact (0.93 for worst case) with high ambient ozone levels (0.2 ppm). Average NO2/NOx ratios for all high ozone cases studied were 0.76-0.9. The reactive model predicts significantly higher ground level NOx impacts from the six plants. These results indicate that the threshold short-term NO2 NAAQS level requiring NOx flue gas treatment technology could increase by 40%. The previous study indicated that most of the six plants could meet a 500 microgram/cu m short-term NO2 standard using NOx combustion modification techniques (50% NOx control); this study indicates NOx flue gas treatment technology (90% control) may be required on these plants to meet a 750 microgram/cu m standard, and most certainly for 500 micrograms/cu m.

EXECUTIVE SUMMARY

The 1977 Amendments to the Clean Air Act required the Environmental Protection Agency (EPA) to establish a short-term National Ambient Air Quality Standard for NO_2 or to show that such a standard is unnecessary. If a short term NO_2 ambient standard is established, it is uncertain what level of NO_x emission controls would be required from stationary combustion sources to attain and/or maintain compliance with the ambient standard. EPA's Industrial Environmental Research Laboratory at Research Triangle Park began to assess this issue in the report, Impact of Point Source Control Strategies on NO_2 Levels, EPA-600/7-78-212, November 1978. This study is a follow-on to that effort.

In the previous study, the major uncertainty was the extent of conversion of NO_x emissions (which are primarily NO) to NO_2 at ground level. The assumption was made of uniform, fixed NO_2/NO_x ratios of 0.5 for summer and 0.25 for winter. In the follow-on study, a reactive Gaussian plume model using the photostationary state approach was developed and used to determine the relationship of ground level NO_2 to NO_x emissions in plumes from six large power plants in the Chicago AQCR. It was found the above assumptions of uniform NO_2/NO_x ratios were not generally applicable to large scale problems. Significantly higher NO_2/NO_x ratios at the point of maximum plume impact can occur under worst case conditions. Plume NO_2/NO_x ratios as high as 0.93 were found for the summer AM case (C stability, 5 m/sec wind speed - worst case in previous study) with high ambient ozone levels. Average NO_2/NO_x ratios for all high ozone cases studied ranged from 0.76 to 0.9. Ozone is the most important factor affecting NO_2/NO_x ratios. Other factors influencing the ratio are wind speed and stability class.

If the higher summer AM ratios were applied to the 1985 results of the previous study, significantly higher maximum ground level NO_2 impacts from the six plants would be predicted. These plant impacts are as follows:

Maximum Ground Level NO_2 Impact Due to Plant
($\mu g/m^3$)

Plant	Previous Study	Reactive Model
Bailly (Northern Indiana Public Service)	754	1357
Will County (Commonwealth Edison)	710	1078
Waukegan (Commonwealth Edison)	524	922
Joliet (Commonwealth Edison)	998	1497
Fisk (Commonwealth Edison)	379	652
Bethlehem Steel	1182	1182

The new results indicate that, for these conditions, the threshold short-term NO_2 standard level where NO_x flue gas treatment becomes necessary could increase by at least 40 percent. For the above plants, the previous study indicated that most could meet a 500 $\mu g/m^3$ short-term NO_2 standard with combustion modification techniques for NO_x control (50 percent NO_x reduction). The reactive study indicates that combustion modification may be insufficient to meet a 750 $\mu g/m^3$ standard and that NO_x flue gas treatment technology (90 percent NO_x control) would almost certainly be required on these units to meet a 500 $\mu g/m^3$ standard. Cases of interaction of several power plant plumes were also studied with similar results and conclusions. Thus, it appears that a short-term NO_2 ambient air quality standard could require stringent NO_x controls on new and existing stationary combustion sources.

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1.0 INTRODUCTION

Nitrogen oxides react with numerous chemical pollutants in the atmosphere. Consequently, simulation of NO_x reactions is an important and complicated problem. The most important reactions im most photochemical situations concern NO, NO_2, O_3, and hydrocarbons in the presence of sunlight. Sunlight causes NO_2 to break down to an NO molecule and an oxygen atom. This oxygen atom combines with an O_2 molecule to form ozone, which then combines with NO to form NO_2 and O_2. Thus, oxygen atoms tend to "trade off" between NO and O_2.

The process becomes much more complicated when hydrocarbons are considered. The mechanism here seems to be that HC molecules present reaction "paths" for the production of NO_2 from NO which do not involve the breakdown of O_3. Thus, a surplus of O_3 builds up from the dissociation of NO_2 and the subsequent reformation of O atoms with O_2 molecules. This explains the heavy buildup of ozone in the presence of large hydrocarbon concentrations.

All of these mechanisms (and many others) enter into the modeling of NO_x in the atmosphere. In addition, the chemical pollutants are being advected and diffused by wind and turbulence in the atmosphere. In general, large numerical computer models are required to simulate atmospheric chemistry. However, these models are generally very expensive and difficult to use.

One recourse available to the modeler is to utilize the simpler and less expensive Gaussian plume model. This type of model has enjoyed great success in modeling the advection and diffusion of pollutants in the past. It offers an analytical closed-form solution to the diffusion equation often used to model

advection and diffusion of inert pollutants. As long as the ground surface in the area to be modeled is not too irregular, and the wind field is homogenous and wind shear is not too large, the Gaussian model is usually adequate for inert chemical species. However, the diffusion equation for which the Gaussian formulae are derived are not valid when the species are reactive. The chemical reactions introduce nonlinearities into the diffusion equation which make analytical solutions impossible.

In modeling NO_x, the nitrogen atoms are usually assumed to be present only in NO or NO_2. Consequently, it is permissible to consider the sum of these concentrations, or identically the concentration of NO_x, to be inert. Thus, NO_x may be modeled by a Gaussian plume formula. This was done by Radian in a previous study for EPA, Eppright et al, Impact of Point Source Control Strategies on NO_2 Levels, EPA-600/7-78-212, November 1978.[1]

In this case, the difficulty is assessing the proper ratio of NO to NO_2 or, identically, the ratio of NO or NO_2 concentrations to total NO_x concentrations. In the above previous study a constant ratio was assumed for all parts of the plume, meaning essentially that both NO and NO_2 concentrations were described by Gaussian formulae. Moreover, the ratio of NO_2 to NO_x in the plume was assumed based on ambient data to be either 1/2 (0.5) in summer or 1/4 (0.25) in winter. The purpose of this study was to develop a more sophisticated treatment of the photochemistry in order to investigate the applicability of these ratios.

In this study, several of the cases in the previous report were analyzed using the reactive model described in this report. Days with high ozone concentrations were identified and meteorological conditions and ambient NO, NO_2, and ozone concentrations were developed. The cases were modeled using the above data for both high (0.2 ppm) and low (0.1 ppm) ozone concentrations. Also, interaction of sources was studied to a limited extent.

2.0 CONCLUSIONS

The reactive model was run for several cases involving six power plants in the Chicago AQCR. A range of meteorological conditions was identified for days with high ambient ozone concentrations. Meteorological conditions were varied in order to study the surface NO_2/NO_x ratios due to the power plants under conditions when a short-term NO_2 standard might be violated. Results for individual power plants are shown in Appendix D and are discussed in Section 4.3.3. From these results the following conclusions concerning the cases studied were drawn:

- NO_2/NO_x ratio for the plume at the point of highest ground level concentration increases as the background ozone concentration increases. Ozone probably has the most influence on the ratio because for higher ozone levels, larger fractions of NO_x are converted to NO_2. According to the theory used in the modeling approach, the total NO_x concentration ($NO + NO_2$) is independent of background ozone concentration.

- For a given wind speed, as the atmosphere becomes more stable over the range of stabilities studied, the NO_2/NO_x ratio increases.

- For a given stability class studied, the NO_2/NO_x ratio decreases as wind speed increases.

- For a given stability class, the distance of the NO_x peak from the stack decreases as wind speed increases. This is a general characteristic of Gaussian dispersion models.

It should be noted that these conclusions are valid only for peak concentrations. At other locations within the plume, different NO_2/NO_x ratios will occur. For example, the NO_2/NO_x ratio increases as cross wind distance from the plume centerline increases although the total concentration of NO_x is reduced over the same distance.

It is also worthwhile to mention that most of those conclusions can be anticipated from the knowledge that (a) as NO_x increases, with a given O_3 background, less conversion of total NO_x to NO_2 occurs, meaning the ratio of NO_2/NO_x decreases, and (b) given a fixed total NO_x value, as O_3 increases so does the NO_2/NO_x ratio. Given these facts, which are derived from the results of the Technical Discussion (Part 4.0), the major conclusion which might not be expected is that, for a given stability class, the NO_2/NO_x ratio decreases as wind speed increases. This is probably due to the fact that an increasing wind speed will lower the plume height, so that the maximum NO_x concentration will be raised, and thus the NO_2/NO_x ratio will be decreased.

It was also found that plant plume interactions are still potentially significant contributors to high ambient NO_2 concentrations. The reactive model predicts that plume interactions may indeed occur over reasonably long distances, depending upon meteorological conditions. Results for power plant interaction cases are shown in Appendix E and are discussed in Section 4.3.4.

For individual plants, ratios of NO_2/NO_x in the plumes at points of peak concentration were found to vary between 0.19 and 0.80 for low backgound ozone concentrations and from 0.46 to 0.93 for high ozone concentrations. Results for the latter case are shown in Table 1. They are considerably higher than the ratio

of 0.5 assumed for summer conditions in the previous study.[1] The results of the earlier study, shown in Appendix D, indicate that previous worst cases occurred for summer A.M., C stability, 5 m/sec wind speed. These conditions are very similar to those used in the present study (C stability, 4.5 m/sec) except for mixing height.* Thus, for coincident high ozone and NO_x, it appears that the NO_2/NO_x ratio in the plume can be significantly higher than 0.5.

For the six plants studied using the reactive model (1985 emissions levels), the summer A.M. NO_2 concentrations from the previous study (ratio of 0.5) were reapportioned using the new NO_2/NO_x ratios. Non-power-plant ratios were assumed to remain at 0.5. The results are shown in Table 2. These are the short-term results which would have been obtained in the previous study had higher NO_2/NO_x ratios for the power plants been used as appears to be warranted by the results of the latest reactive study.

The new results indicate that, for these conditions with concurrent high ozone levels, the threshold short-term NO_2 standard level where flue gas treatment (FGT) for NO_x becomes necessary could increase by at least 40 percent, i.e., if 500 $\mu g/m^3$ were the threshold level under the old study, 750 $\mu g/m^3$ could be the new threshold level. For the above plants, the previous study indicated that most could meet a 400 $\mu g/m^3$ short-term standard with combustion modification techniques for NO_x control. The reactive sutyd indicates that combustion modificamay be insufficient to meet a 750 $\mu g/m^3$ standard and that NO_x flue gas treatment technology would almost certainly be required

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* The theoretical analysis in Section 4.2 indicates, however, that increased NO_x concentrations due to reduced mixing heights will still result in plume NO_2/NO_x ratios significantly higher than 0.5 under high ozone conditions (e.g. 0.2 ppm).

TABLE 1.

OVERALL PLUME NO_2/NO_x RATIOS AT POINT OF PEAK CONCENTRATION OBTAINED FROM REACTIVE MODEL - HIGH OZONE CASE

Stability	Range In Wind Speed Studied	NO_2/NO_x Ratio		
		Min	Max	Avg.
B	1-3 m/sec	.46	.90	.76
C	3-6 m/sec	.45	.91	.78
D	6-8 m/sec	.77	.93	.90

(Note: Bethlehem Steel showed consistently lower ratios than all other power plants and thus tended to reduce the average ratio.)

TABLE 2. EFFECT OF NEW NO_2/NO_x RATIOS ON RESULTS OF PREVIOUS STUDY - SUMMER A.M., COINCIDENT HIGH OZONE CASE

	As Reported in Previous Study				As Modified Based on Results of Latest Study			
Plant	Plant Plume NO_2/NO_x Ratio	Total NO_x	Plant NO_2	Total NO_2	Plant Plume NO_2/NO_x Ratio	Total NO_x	Plant NO_x	Total NO_2*
Bailly **	0.5	1696	754	849	0.90	1696	1357	1451
Will Cty +	0.5	1648	710	824	0.76	1648	1078	1193
Waukegan +	0.5	1588	524	794	0.88	1588	922	1372
Joliet +	0.5	2336	998	1168	0.75	2336	1497	1667
Fisk +	0.5	1531	379	766	0.82	1531	652	1039
Beth Stl	0.5	2554	1182	1277	0.50	2554	1182	1277

* Total NO_2 assumes 50 percent conversion of non-power plant NO_x to NO_2.

** Northern Indiana Public Service

\+ Commonwealth Edison

on these units to meet a 500 $\mu g/m^3$ standard. These effects might be further amplified if non-power plant plumes also had higher NO_2/NO_x ratios.

Results of the interaction cases indicate the same effect, namely that NO_x flue gas treatment most probably will be required to meet higher short-term ambient NO_2 standards if plume reactivity is considered. Thus, it appears that a short-term NO_2 ambient air quality standard could require stringent NO_x conctrols on new and existing stationary combustion sources.

3.0 RECOMMENDATIONS

Further study of the application of NO_x control technology to large point sources should be undertaken. While this study essentially agrees with the previous study that large point sources may dominate high short-term NO_2 levels based upon reactive plume modeling, several factors merit further investigation. First, the stack emissions in lb/hr* from each plant were assumed to consist entirely of NO. The effects of NO/NO_x ratio and ozone concentration in the stack upon NO_2/NO_x ratio downwind should be investigated in detail as NO_2 can constitute a significant portion of the effluent from some sources. Second, this study has shown that the downwind NO_2/NO_x ratio is highly dependent upon background ozone concentration and meteorological conditions. In the case of the plants studied, site-specific meteorological conditions related to the lake breeze effect were not considered, although the lake breeze is thought to have contributed significantly to high ozone concentrations on several days during the period studied. More defensible results could be obtained if the meteorological conditions were investigated more thoroughly or if another AQCR without these specific conditions were investigated. Third, a large scale study of plant interactions similar to the previous study should be considered in order to further clarify the extent of power plant NO_2 impact. Fourth, the new reactive model should be investigated with respect to applicability, especially with regard to variations in diffusivity and advection coefficients. Finally, a large scale photochemical model should be used to investigate the effects of point source NO_x control strategies on levels of NO, NO_2, ozone, and other pollutants on an AQCR basis.

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* Government policy is to stress the use of SI units in technical reports. However, for this report, commonly used units will be given. Conversion factors are shown in Appendix A.

Furthermore, cost and performance characteristics of full-scale NO_x flue gas treatment (FGT) control devices should continue to be studied. The effects of these devices on air quality, economics, and system performance should be investigated.

4.0 TECHNICAL DISCUSSION

4.1 An Adapted Gaussian Model

The reactive plume model developed and used in this study will be discussed. This model was an adapted form of the Gaussian dispersion formula. It was found that, although the species NO, NO_2, and O_3 are not inert, some linear combinations of these species' concentrations act as they were inert[2,3,4]. In addition, reactions between these particular species are generally fast enough to assume they are in equilibrium. This phenomenon will be discussed in greater detail in Section 4.2. The importance of these two observations is that they allow the determination of closed form solutions rather than requiring numerical solutions for the concentrations of these three species when they are the only three pollutants present.

Of course, this last condition is not usually fulfilled. The presence of hydrocarbons in the atmosphere causes a slow buildup of ozone which interacts with NO to form NO_2, as mentioned before. Thus the (NO, NO_2, O_3) system is not closed. However, the ozone buildup is so gradual that for a given short-term observation, the O_3 acts as a background concentration. Thus, when O_3 background concentrations are available, the simulation mechanism described here will be a reasonable approximation for short-term analyses.

4.2 The Reactive Gaussian Model

4.2.1 Background

The reactive Gaussian computer model used was a modified version of a Gaussian dispersion model. Whereas most Gaussian

models are non-reactive, the version used in this study reflects three of the major photochemical reactions known to occur in the atmosphere. These three reactions are described as follows:

$$NO_2 + h\gamma \rightarrow NO + O;\ k_1 \text{ (depends on sunlight)}, \quad (1)$$

$$O + O_2 \rightarrow O_3;\quad k_2 = 2.33 \times 10^{-5} ppm^{-2}\ min^{-1} \quad (2)$$

$$NO + O_3 \rightarrow NO_2 + O_2;\ k_3 = 2.95 \times 10\ ppm^{-1}\ min^{-1} \quad (3)$$

Since the reaction in equation (2) occurs quite rapidly, equations (1) and (3) dominate the chemistry.

These equations are by no means the only photochemical processes which occur in the atmosphere. Certainly reactions involving hydrocarbons, CO_2, and H_2O contribute heavily to the photochemical problem. However, these three reactions, when incorporated into an atmospheric dispersion model, can be used to show short-term trends in the major photochemical species in NO, NO_2, and O_3.

The use of Gaussian model to predict dispersion and advection processes involves other difficulties apart from not dealing with hydrocarbons. Modern numerical models are better equipped to describe the complex structure of the lower atmosphere, and in addition, are better predictors of atmospheric mechanisms in complex terrain. Moreover, the major advantage of numerical models is their ability to simulate the chemical mechanisms which occur in the atmosphere because the concentrations of chemical species at any point in space and time are functions of the reactions which took place prior to the time considered. Thus, in order to find the concentration of NO_2 at a given time and place in the atmosphere, one must solve for the concentrations of all three species, NO, NO_2 and O_3 for all times prior to that considered, and for all locations in space from which

pollutants may diffuse or advect to the point in question. This methodology is ideally suited for numerical cell models, since they already employ a reiterative scheme in determining the wind flow. The major difficulty with numerical models is their extremely long solution time and attendant expense. In addition, the complexity of the numerical approach makes it difficult to get any insight into the physical mechanisms which can be applied generally.

The model developed for this study uses the photostationary state relationship [2, 3] to obtain an analytical solution to the species concentrations, while largely incorporating the chemical processes described in reactions (1) to (3). The analytical nature of the model allows a very fast computation time, and also allows some fairly general statements to be made concerning the chemical processes.

As was previously mentioned, the reason that a Gaussian model is not directly applicable to the species NO, NO_2, and O_3 is that they are not inert. Their reactions introduce nonlinearities into the diffusion equations for the concentrations which prohibit their expansions as Gaussian curves.

However, consider the case of a closed volume with interacting species which are not in equilibrium. Though the molecular concentrations change, the atomic concentrations (obtained by adding the distributions from different species) will not, as a consequence of the conservation of mass. Following Peters and Richards[3] this fact can be exploited to decouple the differential equations which describe the NO, NO_2 and O_3 reactions. Inherent to this decoupling process is the assumption that atomic concentrations are diffused independently of the molecular form in which they are bound. In the case of a single nitrogen atom,

this assumption implies that its movement due to diffusion and turbulence is, for the practical purposes, independent of whether the atom is bound up with a single oxygen atom as NO or two oxygen atoms (NO_2). In other words, given the position of the nitrogen atom at a certain time, its position at a later time will be governed by a distribution law which is independent of the other atoms with which it is bonded. Although this assumption seems questionable on a microscopic level (because of the different molecular weights and different molecular diffusion rates), on a macroscopic level the atmospheric turbulence dominates the diffusion and differences due to molecular type are inconsequential. This principle is generally assumed in modeling any airborne pollutant.

4.2.2 Application to NO_x

Consider the nitrogen atoms in the equations (1), (2), and (3). They can exist either in the form NO or NO_2. Thus, the concentration of nitrogen atoms is given by

$$\psi_1 = [NO] + [NO_2] \tag{4}$$

Now, by the preceding arguments, in the case of a continuous point source at point (0, 0, H) of the coordinate system, in a steady wind u in the x direction it may be seen that

$$\psi_1 = \psi_{10} + \left(\frac{Q_1}{2\pi\sigma_y\sigma_z u}\right) \exp\left(-\frac{y^2}{2\sigma_y{}^2}\right) \exp\left(\frac{-(z+H)^2}{2\sigma_z{}^2} - \frac{(z-H)^2}{2\sigma_z{}^2}\right) \tag{5}$$

where ψ_{10} is the background level of $[NO] + [NO_2]$ and Q_1 is the source strength of $[NO] + [NO_2]$. Other forms of the Gaussian formula are available, but this is sufficient for explanation.

Thus, the nitrogen atomic concentration is given. One might ask if there are any other "composites" of this type. One such group is the "floating" oxygen atoms which may either be "free" (that is, O atoms) or bound up on NO_2 or O_3. These atoms are driven by turbulence and diffusion mechanisms identical to those which influence the nitrogen atoms, so the quantity $[NO_2] + [O_3] + [O]$ is determined by an equation analogous to that for the nitrogen atoms, if it is assumed that equations (1), (2), and (3) are all that apply (i.e., other photochemical processes are ignored). Since $[O]$ is small, due to the reaction speed of equation (2), the combination considered is as follows:

$$\psi_2 = [O_3] + [NO_2] \tag{6}$$

with a distribution of the form,

$$\psi_2 = \psi_{20} + \left(\frac{Q_2}{2\pi\sigma_y\sigma_z u}\right) \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \exp\left(\frac{-(z+H)^2}{2\sigma_z^2} - \frac{(z-H)^2}{2\sigma_z^2}\right) \tag{7}$$

where ψ_{20} is the background level of $[NO_2] + [O_3]$ and Q_2 is the source strength of $[NO_2] + [O_3]$.

It is anticipated that in many cases of interest involving equations (5) and (7), one will have $\psi_{10} = Q_2 = 0$ since the background level of $[NO] + [NO_2]$ will be zero and all the pollutant emitted from the stack will be NO, meaning $Q_2 = 0$. However, equations (5) and (7) will be maintained in their present form for symmetry and generality. Nonzero background levels were used in this analysis.

4.2.3 The Equilibrium Hypothesis

Since ψ_1 and ψ_2 are given in closed form, equations (4) and (6) give two equations in three unknowns. The concentrations [NO], [NO_2], and [O_3] cannot be found without more assumptions.

If the assumption is made that the species [NO], [NO_2], and [O_3] are in equilibrium, then there exist three equations in three unknowns allowing a solution. Choosing [NO] as the species in question,

$$\frac{d}{dt}[NO] = k_1 [NO_2] - k_3[NO][O_3] \tag{8}$$

and for equilibrium to hold, this must equal zero, so

$$\frac{[NO][O_3]}{[NO_2]} = \frac{k_1}{k_3} \tag{9}$$

Combining equations (4), (6), and (9) gives

$$[NO_2] = \frac{\psi_1 + \psi_2 + \frac{k_1}{k_3} - \sqrt{\left(\psi_1 + \psi_2 + \frac{k_1}{k_3}\right)^2 - 4\psi_1\psi_2}}{2} \tag{10}$$

$$[NO] = \frac{\psi_1 - \psi_2 - \frac{k_1}{k_3} + \sqrt{\left(\psi_1 + \psi_2 + \frac{k_1}{k_3}\right)^2 - 4\psi_1\psi_2}}{2} \tag{11}$$

$$[O_3] = \frac{-\psi_1 + \psi_2 - \frac{k_1}{k_3} + \sqrt{\left(\psi_1 + \psi_2 + \frac{k_1}{k_3}\right)^2 - 4\psi_1\psi_2}}{2} \tag{12}$$

Thus, the species concentrations are available in closed form for a short-term solution.

These are the solutions for the NO, NO_2 and O_3 concentrations given the assumption of equilibrium. There are some difficulties with this assumption, as are discussed in references (2), (3), and (4). In general, non-homogeneities in the plume and background concentrations seem to cause some departures from equilibrium, but it is thought that this is largely a result of concentration measurements which are averaged over time.[2] Until more is known about these processes, the equilibrium assumption still appears to be a very reasonable and practical approach.

It should be mentioned here that in applying equations (10) through (12), it is not necessary to actually calculate the new composite functions ψ_1 or ψ_2. Instead, it is sufficient to observe that by the arguments of the preceding section the same results were obtained for the atomic concentrations regardless of whether the species was considered inert. Thus, the existing Gaussian model can be modified and used to calculate the "inert" species concentrations at any given point in space, and then these quantities transformed to get the new equilibrium concentrations.

Thus, if the existing model gives $[NO]_o$, $[NO_2]_o$, and $[O_3]$ as the "inert" concentrations at a point (x, y, z), then from equations (4) and (6)

$$\psi_1 = [NO]_o + [NO_2]_o \tag{13}$$

$$\psi_2 = [O_3]_o + [NO_2]_o \tag{14}$$

Equations (10) through (12) may then be applied directly to ψ_1, ψ_2 to transform the "inert" concentrations to actual concentrations. This procedure, shown in Figure 1, was used in the present study.

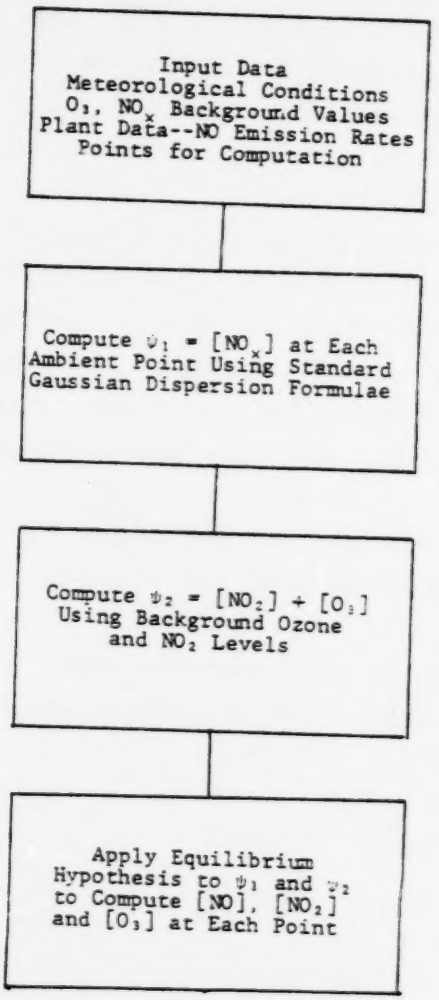

Input Data
Meteorological Conditions
O_3, NO_x Background Values
Plant Data--NO Emission Rates
Points for Computation
Compute $\psi_1 = [NO_x]$ at Each Ambient Point Using Standard Gaussian Dispersion Formulae
Compute $\psi_2 = [NO_2] + [O_3]$ Using Background Ozone and NO_2 Levels
Apply Equilibrium Hypothesis to ψ_1 and ψ_2 to Compute [NO], $[NO_2]$ and $[O_3]$ at Each Point

FIGURE 1. PROCEDURE FOR COMPUTING SHORT-TERM CONCENTRATIONS OF NO, NO_2, AND O_3

4.3 Reactive Model Results

In the previous section it was shown that an analytic solution to the short-term reactive plume problem could be reached. The methodology developed was tested both theoretically and practically. These results will now be discussed.

4.3.1 Interactions Between NO, NO_2, O_3 In a Plume

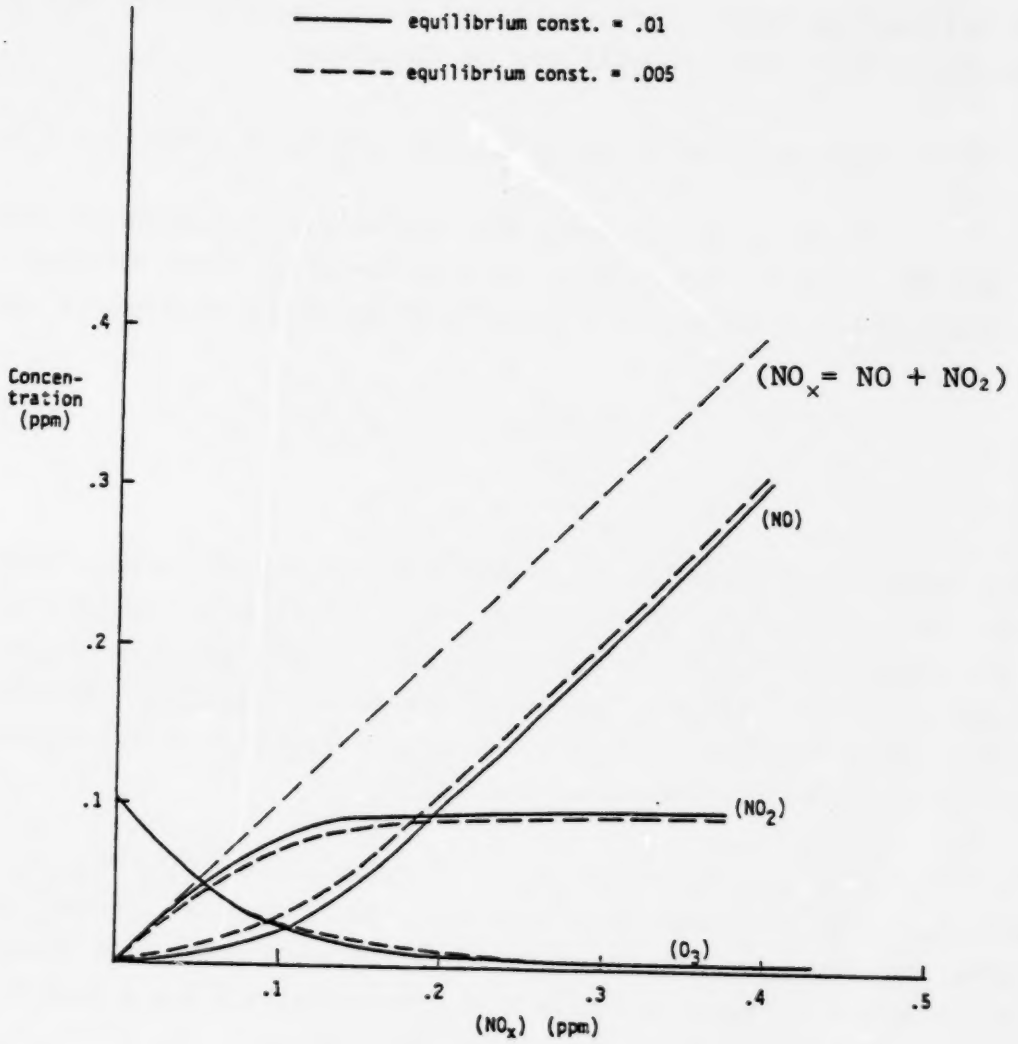
It is useful to consider the relative concentrations of NO, NO_2, and O_3 which exist in a plume when these species are in equilibrium. Using the equilibrium relation previously derived,

$$\frac{[NO][O_3]}{[NO_2]} = \frac{k_1}{k_3} = k \qquad (15)$$

and the above methods it is possible to obtain the short-term concentrations of NO, NO_2, and O_3 as a function of $[NO_x]$. Assuming an initial background concentration of 0.1 ppm for ozone, and assuming k=0.01, Figure 2 shows these concentrations. Notice that if K is changed to 0.005 the curves are virtually unchanged, so exact values of k are not crucial.

Another informative way of viewing the NO, NO_2, O_3 interactions is by considering a typical plume. Figure 3 shows the three species' surface concentrations at various points downwind from a stack. Figure 4 shows the concentrations as a function of crosswind distance from the plume centerline.

A third observation about the relative NO, NO_2, and NO_x concentrations is that there is usually some ambiguity about the proportions of these species emitted from the stack. Thus, often



02-4241-1

FIGURE 2. SPECIES CONCENTRATIONS OF NO, NO_2, AND O_3 versus NO_x CONCENTRATIONS

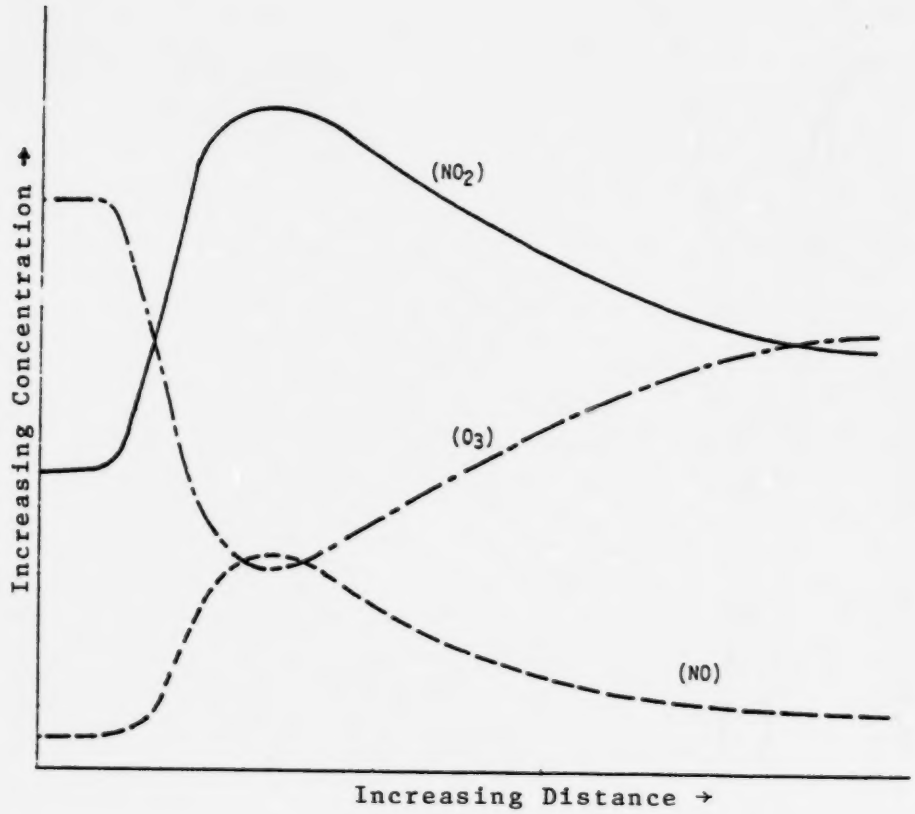


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FIGURE 3. TYPICAL SURFACE CONCENTRATIONS OF NO, NO_2, AND O_3 DOWNWIND FROM STACK

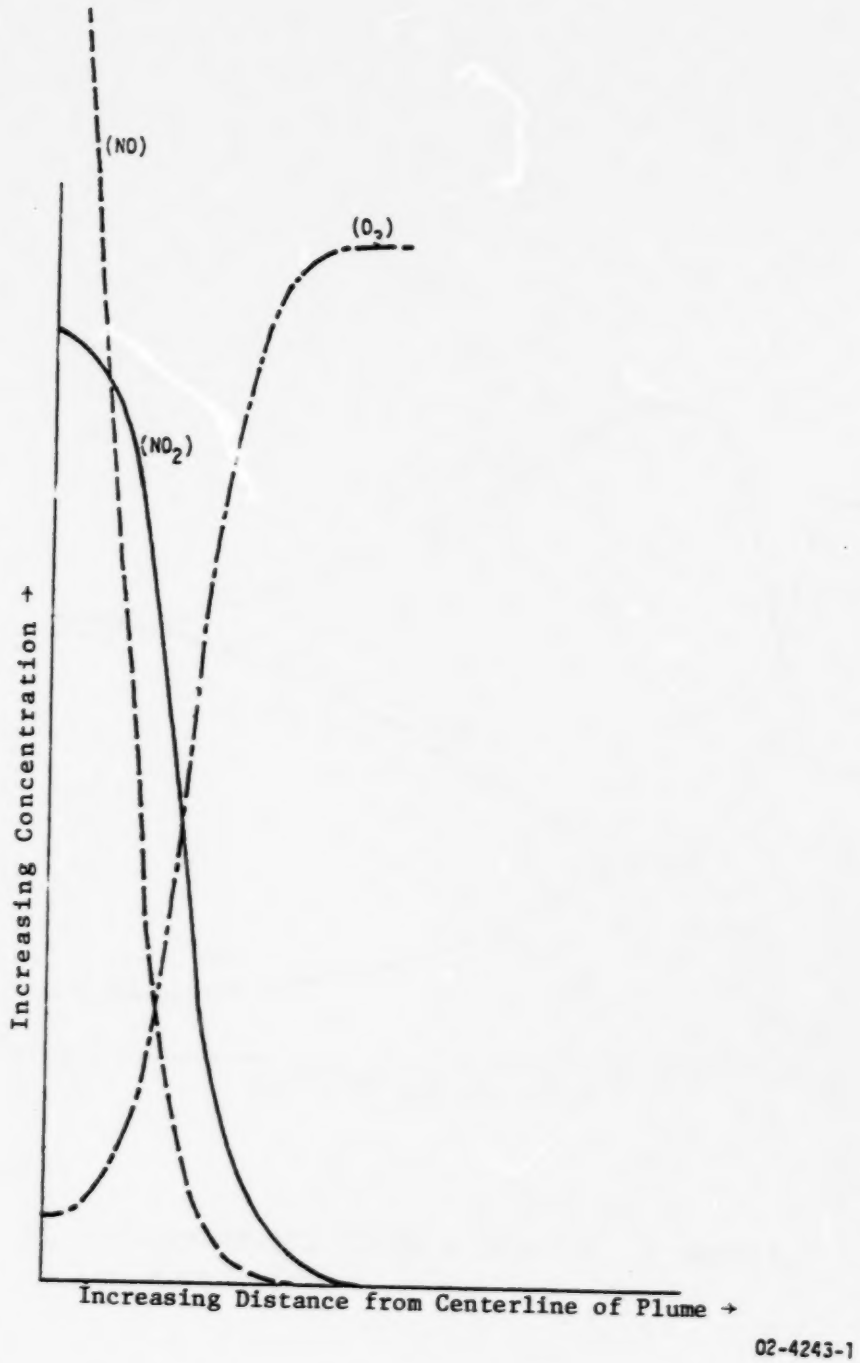

FIGURE 4. TYPICAL SPECIES CONCENTRATIONS ACROSS WIDTH OF PLUME

measurements of NO_x emissions do not discriminate between NO and NO_2. However, with the huge concentrations of NO_x within the stack, Figure 2 shows that NO will prevail. Indeed, NO is generally assumed to comprise 95 percent or more of the NO_x present in stack emissions. This is important because it allows the simplifying assumption that plant NO_x emissions are comprised entirely of NO.

4.3.2 Power Plant Reactive Plume Modeling

Computer runs using the new reactive model were made for six power plants in the Chicago AQCR under a large variety of meteorological conditions to determine the ratios of NO_2 to NO_x concentrations. Three types of cases were investigated, all of which were based on concentrations downwind from the stacks.

(1) First, the total NO_x concentration was calculated, assuming a constant background concentration of NO_x of 0.05 ppm, which is a representative value.

(2) A low-ozone situation was simulated. This run used the same background value of NO_x as (1), but the ratio of background NO_2 to NO_x was adjusted to give equilibrium. The ozone level was set at 0.1 ppm.

(3) A high-ozone background was simulated. Here the ozone level was set at 0.2 ppm. The NO_x level was kept at 0.05 ppm, but again the background NO-NO_2 split was adjusted for equilibrium.

In each case the following results were obtained:

- Downwind distance of NO_2 and NO_x peaks
- NO_2 and NO_x concentrations
- Ratio of NO_2 to NO_x for the plume only

These cases were evaluated for given meteorological conditions and power plant outputs.

4.3.2.1 Meteorology

Ambient atmospheric conditions were developed from actual 1975 Chicago data. Seven days with extremely high ambient O_3 levels at up to seven continuous monitor sites were identified.* Ambient ozone maximum levels on these days ranged from slightly over 0.1 ppm to nearly 0.25 ppm. A synopsis of Chicago meteorological conditions for these days is given in Appendix B. In general, meteorological conditons associated with these days were as follows:

Sunny and warm with no cloud cover, haze, or thin high clouds

High pressure and/or presence of a cool front

- Temperature in high 80's or low 90's
- Wind speeds about 10 mph or less
- B or C stability
- Unlimited mixing or high mixing heights*

*It was assumed that high ambient O_3 levels would result in high NO_2 levels for power plants.

The "stability" of the atmosphere refers to its ability to disperse pollutants. Mixing height in the thickness of a ground-gased layer through which pollutant mixing and dispersion occurs.

In addition, on several days conditions were favorable for onshore penetration by the lake breeze or lake breeze enhancement of meteorological conditions in the areas with the highest ambient concentrations.

For each of the above three case types (representative low O_3, high O_3), nine meteorological situations were simulated. Type B stability was run with wind speeds of 1, 2, and 3 m/sec. Type C wind speeds considered were 3, 4.5, and 6 m/sec. Type D stabilities had wind speeds of 6, 7, and 8 m/sec. The temperature was 80°F, and there was unlimited mixing. As previously stated, these conditions appear to be conducive to high ambient ozone levels in Chicago, although further investigations should also address lake breeze effects.

4.3.2.2 Power Plants

The following six Chicago-area coal-fired power plants were investigated in this study:

- Bailly (Northern Indiana Public Service)
- Will County (Commonwealth Edison)
- Waukegan (Commonwealth Edison
- Joliet (Commonwealth Edison)
- Fisk (Commonwealth Edison)
- Bethlehem Steel

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*In the previous study results (Appendix C), mixing heights ranged from 200-800 meters. Theoretically, these lower mixing heights are usually conducive to high ozone formation. The ozone incident studied may have resulted from other factors (such as lake breeze effect) despite unlimited mixing or high mixing heights.

The locations of these plants are shown in Figure 5. In the previous Chicago study, these six plants had high ambient NO_x and NO_2 levels predicted; these levels are shown for 1975 in Appendix C.

NO_x emissions for 1975 for these six plants were estimated in the previous study and are shown in Table 3. These emissions were assumed to be entirely NO at the stack orifice; the values in Table 3 were converted to reflect the change in atomic weight. It was also assumed that no ozone was emitted from the stacks.

4.3.3 Model Results--Individual Plants

Detailed model results for the six plants studied are shown in Appendix D. Ratios of NO_2/NO_x at the point of highest ground level concentration ranged from 0.19 to 0.80 for low background ozone concentrations and from 0.46 to 0.93 for high ozone concentrations. As an example, results for the Will County plant are shown in Table 4. From the results, the following conclusions concerning the cases studied were drawn:

- the NO_2/NO_x ratio for the plume at the point of highest ground level concentration is related to background ozone concentration. Ozone probably has more influence on the ratio than any other factor.

- for a given wind speed, as the atmosphere becomes more stable over the range of stabilities studied, the ratio of NO_2/NO_x increases.

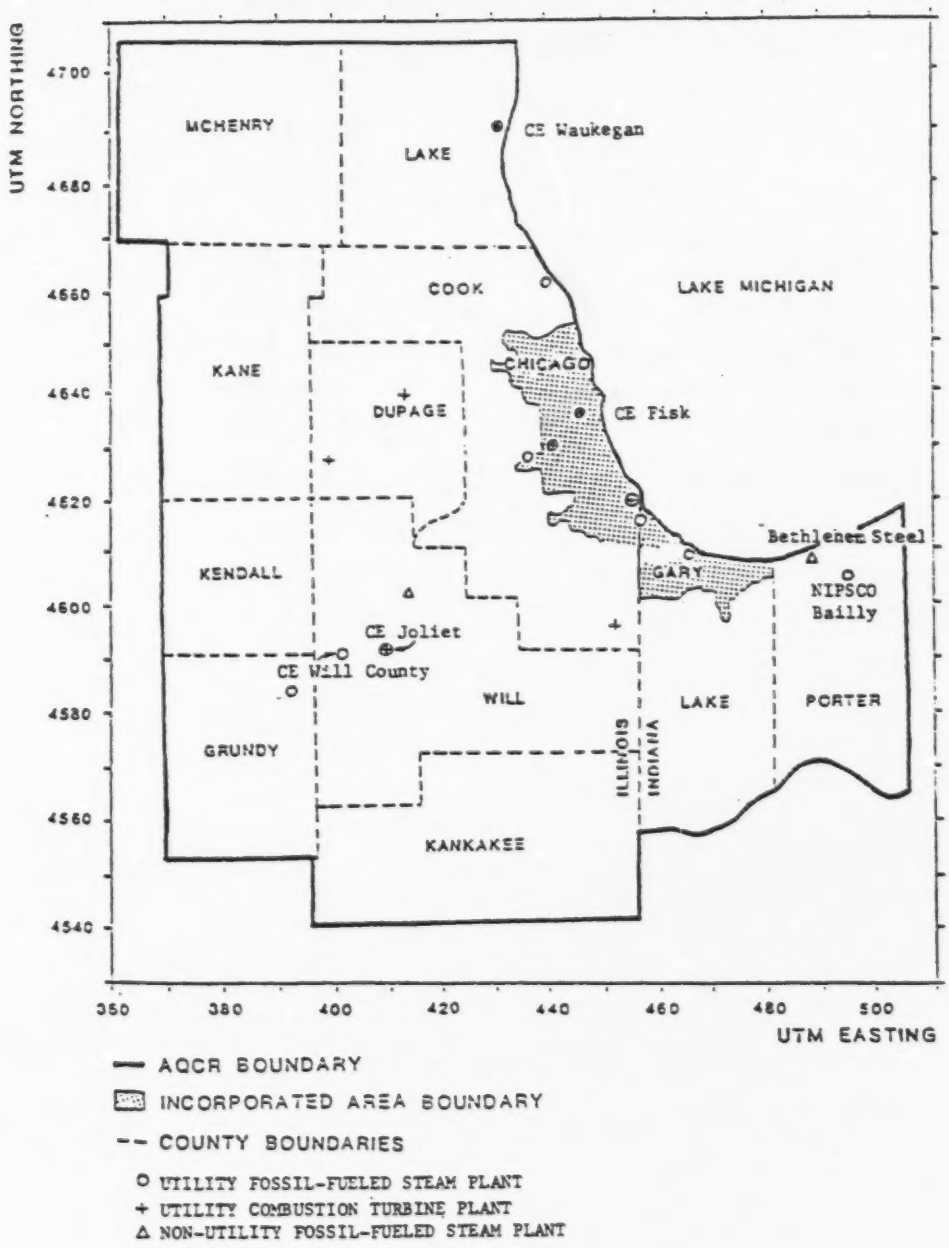

FIGURE 5. POWER PLANTS IN CHICAGO AQCR

(Plants Used Are Identified)

TABLE 3. 1975 ESTIMATED NO_x
FROM SIX POWER PLANTS STUDIED
(NO_x AS NO_2)

Plant	NO_x as NO_2* (lb/hr)
Bailly	14,960
Will County	15,126
Waukegan	13,414
Joliet	24,606
Fisk	7,298
Bethlehem Steel	10,135

*Full Load.

TABLE 4.

MODEL RESULTS FOR WILL COUNTY PLANT

STABILITY	WIND SPEED METERS/SEC	DISTANCE OF NO_x PEAK FROM 1ST STACK (m)	NO_x IN EXCESS OF BACKGROUND NO_x (ppm)	LOW OZONE BACKGROUND			HIGH OZONE BACKGROUND		
				NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 / EXCESS NO_x	NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 / EXCESS NO_x
				$\mu g/m^3$	ppm	(ppm)	$\mu g/m^3$	ppm	(ppm)
B	1	11600	.152	133	.072	.48	240	.130	.85
B	2	4000	.220	144	.078	.35	305	.165	.75
B	3	2800	.257	147	.080	.31	325	.180	.69
C	3	6400	.184	140	.076	.41	275	.150	.81
C	4.5	4800	.214	143	.078	.36	301	.160	.76
C	6	4000	.229	145	.078	.34	311	.170	.74
D	6	16800	.082	102	.055	.66	138	.075	.91
D	7	14400	.088	106	.058	.65	148	.080	.91
D	8	12800	.093	109	.059	.64	155	.080	.90

Background Concentrations:

Low Ozone Case:

$[O_3]$ = .1 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00455 ppm, $[NO_2]$ = .0455 ppm

High Ozone Case:

$[O_3]$ = .2 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00238 ppm, $[NO_2]$ = .0476 ppm

- for a given stability class, the distance of the NO_x peak from the stack decreases as wind speed increases. This is a general characteristic of Gaussian dispersion models.

It should also be noted that the total $[NO_x]$ value is independent of the concentration of background ozone, so one value of $[NO_x]$ is given for both cases. Also, the NO, NO_2, and NO_x concentrations all peak at the same point in the modeling results, which is again the result of the monotonic dependence of [NO] and $[NO_2]$ on $[NO_x]$ in the model theory, as illustrated earlier in Figure 2.

It also appears that the short-term NO_2 impact of power plants will be significant in many cases. Moreover, it should be noted that, for the cases studied, the net percentage of NO_2 at the point of greatest impact may be greater than the value assumed in the previous study, depending on background ozone concentration. This would result in greater power plant impacts and, thus, a greater need for flue gas treatment to meet a given short-term NO_2 standard.

4.3.4 Model Results--Interaction Case

The interaction of plumes from eight power plants along the Chicago Sanitary and Barge Canal was also studied. Resulting ground-level NO_2 concentrations along a line from Collins to Fisk for the meteorological conditions discussed in Section 4.3.2.1 are shown in Appendix E. The case studied which resulted in the highest NO_2 concentrations was B stability, high ozone; these results are shown in Figure 6 along with the NO_2/NO_x ratio for a wind speed of 1 m/sec.

When NO_x concentrations from a given plume are calculated in a Gaussian model the predictions are questionable beyond 50 km, and since the total distance modeled in this study was of the order of 100 km, this might cause some concern. However, the figures clearly show that the most important interactive effects occur within 50 km of each stack (where the Gaussian approach is reasonable).

Comparison of these results with others in Appendix E indicates that strong plume interactions may indeed occur. The degree of interaction and the resulting ground level NO_2 concentrations at any point was found to be a result of the following factors:

- background ozone concentration
- stability class
- wind speed (and direction)

In addition, the degree of interaction is highly dependent upon power plant loading; this was not investigated in this study although it was addressed to some degree for "typical" cases in the previous study. The cases investigated in this study assumed that all plants were operating at full load, a case which amy not occur during most of the year. However, this case is more likely to occur during the meteorological conditions addressed in this study, since high ozone conditions are generally associated with hot weather and strongly correlate with summer peak loads caused by high air-conditioning demand. For example, the Commonwealth Edison 1975 summer peak load of 12,305 megawatts occurred on August 1 between 1 and 2 pm; August 1 was one of the days studied because of high ozone levels. Moreover, the Commonwealth

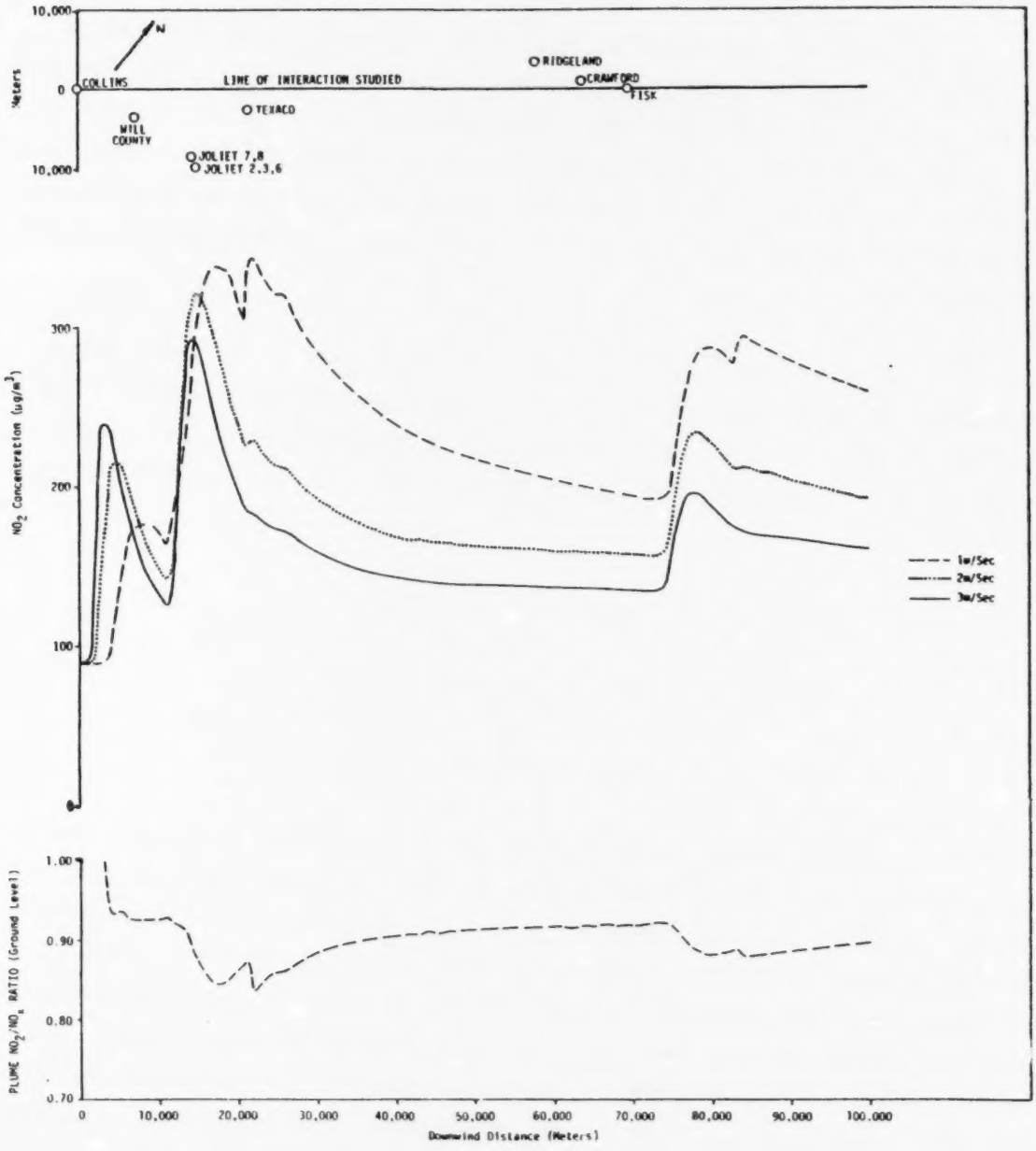

FIGURE 6. NO_2 CONCENTRATIONS AND $NO_2/NO\times$ RATIO FOR AN EXAMPLE INTERACTION CASE

Edison summer peak period in 1975 was from 14 July to 30 August, a period including all but two of the days with very high ozone levels. Hence, it is not unreasonable for generalized analysis to consider cases with power plants at full load or nearly full load, especially if the system peak correlates well with high measured ambient ozone levels.*

* Because of its general nature, this analysis did not attempt to include actual plant loadings. More specific analysis of actual case days should include actual loadings and emission rates.

REFERENCES

1. B. R. Eppright, et al, Impact of Point Source Control Strategies in NO_2 Levels, EPA-60077-78-212, November 1978.

2. Bilger, R. W. (1978) "The effect of admixing fresh emissions on the photostationary state relationship in photochemical smog." Atmospheric Environment 12, 1109-1118.

3. Peters, L. K. and Richards, L. W. (1977) "Extension of atmospheric dispersion models to incorporate fast reversible reactions." Atmospheric Environment 11, 101-108.

4. Kewley, D. J. (1978) "Atmospheric Dispersion of a Chemically Reacting Plume." Atmospheric Environment Vol. 12 pp. 1895-1900.

5. Seinfeld, J. H. (1975) Air Pollution: Physical and Chemical Fundamentals, McGraw-Hill, Inc.

APPENDIX A

SELECTED CONVERSION FACTORS

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SELECTED CONVERSION FACTORS

New Units	Equal	Old Units	Multiplied By
Joules		Million BTU (MMBTU)	1.054×10^{9}
Metric Tons/ Year		Tons/Year	0.907
m/sec		knots	0.514
g/sec		lb/hour	0.125
m^3		Thousand Cubic Feet (MCF)	28.3
m/sec		mph	0.447
kilometer		mile	1.609
g/joule		lb/MMBTU	4.304×10^{-7}
kPa		psia	0.143

APPENDIX B

SUMMARY OF METEOROLOGICAL CONDITIONS FOR CASE DAYS STUDIED

APPENDIX B

SUMMARY OF METEOROLOGICAL CONDITIONS FOR CASE DAYS STUDIED

07/01/75
- -- Sunny; warm; no precipitation in area.
- -- Weak pressure gradient, on west part of broad high pressure system.
- -- Southeasterly to southerly gradient flow over area. Wind speed 3-12 mph.
- -- Favorable for lake breeze from Lake Michigan to reach well into Chicago.
- -- C stability; temperature mid-80's.
- -- Mixing heights 6700-6800 ft.

07/02/75
- -- Mostly sunny, with mostly high, thin clouds; warm; and no precipitation in area.
- -- Weak pressure gradient in morning, becoming somewhat stronger in afternoon, as broad high pressure system shifted slowly to position southwest through southeast of Chicago.
- -- Southwesterly to westerly gradient flow over area. Wind speed 3-9 mph.
- -- Not very favorable for lake breeze to extend onshore on west side of Lake Michigan.
- -- B stability; temperature upper 80's.
- -- Mixing heights 6500-6800 ft.

07/30/75 -- Sunny; warm; no precipitation; hazy.

-- High pressure ridge over area, with center in northeastern U.S.

-- Easterly gradient wind over most of area. Wind speed 3-13 mph.

-- Favorable for lake breeze enhancement of easterly winds to occur well into Chicago.

-- C stability; temperature lower 90's.

-- Mixing heights 500-5800 ft.

07/31/75 -- Sunny; warm; no precipitation; hazy.

-- High pressure over area, with one center over northern lower Michigan and one in the Middle Atlantic States.

-- Easterly gradient flow, in general, over the area, with a northeast tendency. Wind speed 0-13 mph.

-- C stability; temperature lower 90's.

-- Mixing heights 500-5700 ft.

08/01/75 -- Partly sunny in morning, mostly cloudy in afternoon and night; warm; thundershowers and showers in latter part of afternoon and in evening; hazy in early morning, before thundershowers began in afternoon, and between showers.

-- Cold front moving east from Central and Northern Plains and weak disturbance moving north from lower Mississippi Valley; high pressure shifting slowly southeastward.

-- Generally southerly to southeasterly gradient winds over area, but variable and gusty with disturbed conditions in afternoon. Wind speeds 0-13 mph.

-- Marginal situation for significant penetration of lake breeze into Chicago, but conditions apparently rather complicated during course of day.

-- B to D stability; temperature in lower 90's.

-- Mixing height 4700-5900 ft.

-- NOTE: Cold front did not move through Chicago until the afternoon of 08/02.

08/04/75 -- Sunny; warm; no precipitation.

-- Between two cold fronts, one from Lower Great Lakes to lower Mississippi Valley and one Upper Great Lakes to Central Plains; weak high pressure, centered over northern Missouri.

-- Westerly gradient wind in day, followed by westerly to southwesterly gradient flow in evening and night as second cold front approached from the north. Wind speeds 5-9 mph.

-- Not favorable for lake breeze penetration into Chicago.

-- B to C stability; temperature in upper 80's to lower 90's.

-- Nearly unlimited mixing.

-- NOTE: Cold front passed through Chicago in the morning on 08/05, accompanied by showers and followed by a large, cool high pressure system.

08/11/75 -- Day began clear and very hazy, with increasing high, thin cloudiness in late morning; overcast in afternoon, with thunderstorm activity; warm until mid afternoon.

-- Quasi-stationary front in area, on east-west alignment just north of Chicago; weak pressure gradient, with weak lows in southeast Canada and in Nebraska and a weak high center in northern Wisconsin-Michigan area.

-- Winds variable, but mostly with westerly component; high wind gusts with thunderstorms in mid afternoon. Wind speeds 0-23 mph.

-- Not favorable for lake breeze penetration very far into Chicago or for much duration.

-- B and D stability; temperature high 80's.

-- Mixing heights 8800-9000 ft.

-- NOTE: Front and disturbed, showery weather remained in Chicago area for next four days.

APPENDIX C

PREDICTED 1975 NO_x AND NO_2 LEVELS FOR SIX CHICAGO AREA POWER PLANTS - PREVIOUS STUDY[1] (NON-REACTIVE PLUME MODEL)

NO_x Concentrations ($\mu g/m^3$) at Power Plant Worst Case Point for Bailly

Year: 1975

Study Conditions	Contributor	Wind Direction North	South	East	West
Summer PM 3-9; 80°F Mix Depth =800 m R max =2.5 km NO_2/NO_x = 1/2	Power Plant	300	300	300	300
	CT's	10	10	10	10
	Other Point Sources	0	0	0	7
	Vehicles	3	5	24	35
	Non-Vehicles	0	1	5	8
	Total NO_x	313	316	339	360
	Total NO_2	157	158	170	180
Summer AM C-5; 70°F Mix Depth = 272 m R max = 3.5 km NO_2/NO_x = 1/2	Power Plant	1508	1508	1508	1508
	CT's	100	100	100	100
	Other Point Sources	0	0	0	31
	Vehicles	5	8	7	100
	Non-Vehicles	1	3	2	45
	Total NO_x	1614	1619	1617	1784
	Total NO_2	807	810	809	892
Winter AM C-5; 20°F Mix Depth = 272 m R max = 3.5 km NO_2/NO_x = 1/4	Power Plant	1592	1592	1592	1592
	CT's	100	100	100	100
	Other Point Sources	0	0	0	35
	Vehicles	5	9	8	117
	Non-Vehicles	4	10	6	215
	Total NO_x	1701	1711	1706	2059
	Total NO_2	425	428	427	515

NO_x Concentrations ($\mu g/m^3$) at Power Plant Worst Case Point for Will County

Year: 1975

Study Conditions	Contributor	Wind Direction North	South	East	West
Summer PM B-9; 80°F Mix Depth = 800 m R max = 1.6 km NO_2/NO_x = 1/2	Power Plant	670	676	676	676
	CT's	0	0	0	0
	Other Point Sources	134	128	129	167
	Vehicles	15	4	5	2
	Non-Vehicles	1	1	1	0
	Total NO_x	826	809	811	845
	Total NO_2	413	405	406	423
Summer AM C-5; 70°F Mix Depth = 282 m R max = 3.6 km NO_2/NO_x = 1/2	Power Plant	1419	1419	1419	1419
	CT's	0	0	0	0
	Other Point Sources	135	165	138	146
	Vehicles	41	5	12	3
	Non-Vehicles	6	2	4	1
	Total NO_x	1601	1591	1573	1569
	Total NO_2	801	796	787	785
Winter AM C-5; 20°F Mix Depth = 282 m R max = 3.6 km NO_2/NO_x = 1/4	Power Plant	1498	1498	1498	1498
	CT's	0	0	0	0
	Other Point Sources	148	176	149	157
	Vehicles	48	6	14	4
	Non-Vehicles	43	14	29	10
	Total NO_x	1737	1694	1690	1669
	Total NO_2	434	424	423	417

NO_x Concentrations ($\mu g/m^3$) at Power Plant Worst Case Point for Waukegan

Year: 1975

Study Conditions	Contributor	Wind Direction North	South	East	West
Summer PM 3-9; 80°F Mix Depth = 800 m R max = 2.0 km NO_2/NO_x = 1/2	Power Plant	328	328	328	328
	CT's	53	53	53	53
	Other Point Sources	0	51	2	0
	Vehicles	18	67	0	18
	Non-Vehicles	2	8	1	2
	Total NO_x	401	507	384	401
	Total NO_2	201	254	192	201
Summer AM C-5; 70°F Mix Depth = 282 m R max = 3.6 km NO_2/NO_x = 1/2	Power Plant	1048	1048	1048	1048
	CT's	474	474	474	474
	Other Point Sources	0	193	9	28
	Vehicles	35	188	23	25
	Non-Vehicles	10	44	5	7
	Total NO_x	1567	1947	1559	1582
	Total NO_2	784	974	780	791
Winter AM C-5; 20°F Mix Depth = 282 m R max = 3.6 km NO_2/NO_x = 1/4	Power Plant	1106	1106	1106	1106
	CT's	474	474	474	474
	Other Point Sources	0	135	10	28
	Vehicles	40	219	27	29
	Non-Vehicles	74	326	35	54
	Total NO_x	1694	2260	1652	1691
	Total NO_2	424	565	413	423

NO_x Concentrations ($\mu g/m^3$) at Power Plant Worst Case Point for Joliet 7

Year: 1975

Study Conditions	Contributor	Wind Direction North	South	East	West
Summer PM B-9; 80°F Mix Depth = 800 m R max = 2.6 km NO_2/NO_x = 1/2	Power Plant	247	247	247	247
	CT's	86	86	86	86
	Other Point Sources	4	1	1	8
	Vehicles	24	4	5	2
	Non-Vehicles	2	2	1	1
	Total NO_x	363	340	340	344
	Total NO_2	182	170	170	172
Summer AM C-5; 70°F Mix Depth = 312 m R max = 4.0 km NO_2/NO_x = 1/2	Power Plant	1020	1020	1202	1020
	CT's	219	219	219	219
	Other Point Sources	15	2	3	31
	Vehicles	68	10	11	4
	Non-Vehicles	13	6	6	4
	Total NO_x	1335	1257	1259	1278
	Total NO_2	668	629	630	639
Winter AM C-3; 20°F Mix Depth = 312 m R max = 4.0 km NO_2/NO_x = 1/4	Power Plant	1077	1077	1077	1077
	CT's	219	219	219	219
	Other Point Sources	15	2	3	33
	Vehicles	80	11	13	5
	Non-Vehicles	97	41	48	29
	Total NO_x	1488	1350	1360	1363
	Total NO_2	372	338	340	341

NO_x Concentrations ($\mu g/m^3$) at Power Plant Worst Case Point for Fisk

Year: 1975

Study Conditions	Contributor	Wind Direction North	South	East	West
Summer PM B-9; 80°F Mix Depth =800 m R max =1.4 km NO_2/NO_x = 1/2	Power Plant	383	383	383	383
	CT's	84	84	84	84
	Other Point Sources	2	8	0	74
	Vehicles	98	114	59	104
	Non-Vehicles	18	20	14	17
	Total NO_x	585	609	540	662
	Total NO_2	293	305	270	331
Summer AM C-5; 70°F Mix Depth = 272 m R max = 3.5 km NO_2/NO_x = 1/2	Power Plant	758	758	758	758
	CT's	798	798	798	798
	Other Point Sources	9	36	147	204
	Vehicles	242	312	127	269
	Non-Vehicles	67	84	58	70
	Total NO_x	1874	1988	1888	2099
	Total NO_2	937	994	944	1050
Winter AM C-3; 20°F Mix Depth = 272 m R max = 3.5 km NO_2/NO_x = 1/4	Power Plant	797	797	797	797
	CT's	798	798	798	798
	Other Point Sources	9	39	133	204
	Vehicles	283	366	148	315
	Non-Vehicles	503	627	433	524
	Total NO_x	2390	2627	2309	2638
	Total NO_2	598	657	577	660

NO_x Concentrations ($\mu g/m^3$) at Power Plant Worst Case Point for Bethlehem Steel

Year: 1975

Study Conditions	Contributor	Wind Direction: North	South	East	West
Summer PM B-9; 80°F Mix Depth =800 m R max =1.4 km NO_2/NO_x = 1/2	Power Plant	813	813	813	813
	CT's	0	0	0	0
	Other Point Sources	0	0	0	12
	Vehicles	1	2	3	31
	Non-Vehicles	1	1	2	9
	Total NO_x	815	816	818	865
	Total NO_2	408	408	409	433
Summer AM C-5; 70°F Mix Depth =200 m R max =2.5 km NO_2/NO_x = 1/2	Power Plant	2623	2623	2623	2623
	CT's	0	0	0	0
	Other Point Sources	0	1	0	62
	Vehicles	2	5	7	88
	Non-Vehicles	5	4	2	46
	Total NO_x	2630	2633	2632	2819
	Total NO_2	1315	1317	1316	1410
Winter AM C-5; 20°F Mix Depth = 200m R max = 2.5km NO_2/NO_x = 1/4	Power Plant	2494	2494	2494	4819
	CT's	0	0	0	0
	Other Point Sources	0	1	0	66
	Vehicles	3	5	8	103
	Non-Vehicles	16	42	7	226
	Total NO_x	2513	2542	2509	2889
	Total NO_2	628	636	627	722

APPENDIX D

PREDICTED NO_x AND NO_2 CONCENTRATIONS FOR SIX CHICAGO-AREA POWER PLANTS-- REACTIVE PLUME MODEL

PLANT - BAILLY

STABILITY	WIND SPEED METERS/SEC	DISTANCE OF NO_x PEAK FROM 1ST STACK (m)	NO_x IN EXCESS OF BACKGROUND NO_x (ppm)	LOW OZONE BACKGROUND			HIGH OZONE BACKGROUND		
				NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 / EXCESS NO_x	NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 / EXCESS NO_x
				$\mu g/m^3$	ppm	(ppm)	$\mu g/m^3$	ppm	(ppm)
B	1	-	-	-	-	-	-	-	-
B	2	6400	.102	115	.062	.61	170	.092	.90
B	3	4400	.127	126	.068	.54	207	.112	.88
C	3	10800	.083	102	.055	.67	139	.076	.91
C	4.5	7600	.105	116	.063	.60	175	.095	.90
C	6	6000	.121	124	.067	.56	198	.107	.88
D	6	34400	.032	48	.026	.80	56	.030	.93
D	7	28800	.037	54	.029	.78	64	.035	.93
D	8	24400	.041	60	.032	.78	71	.038	.93

Background Concentrations:

Low Ozone Case:

$[O_3]$ = .1 ppm, $[NO_x]$ = .05 ppm, [NO] = .00455 ppm, $[NO_2]$ = .0455 ppm

High Ozone Case:

$[O_3]$ = .2 ppm, $[NO_x]$ = .05 ppm, [NO] = .00238 ppm, $[NO_2]$ = .0476 ppm

PLANT - WILL COUNTY

STABILITY	WIND SPEED METERS/SEC	DISTANCE OF NO_x PEAK FROM 1ST STACK (m)	NO_x IN EXCESS OF BACKGROUND NO_x (ppm)	LOW OZONE BACKGROUND			HIGH OZONE BACKGROUND		
				NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 EXCESS NO_x	NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 EXCESS NO_x
				$\mu g/m^3$	ppm	(ppm)	$\mu g/m^3$	ppm	(ppm)
B	1	11600	.152	133	.072	.48	240	.130	.85
B	2	4000	.220	144	.078	.35	305	.165	.75
B	3	2800	.257	147	.080	.31	325	.180	.69
C	3	6400	.184	140	.076	.41	275	.150	.81
C	4.5	4800	.214	143	.078	.36	301	.160	.76
C	6	4000	.229	145	.078	.34	311	.170	.74
D	6	16800	.082	102	.055	.66	138	.075	.91
D	7	14400	.088	106	.058	.65	148	.080	.91
D	8	12800	.093	109	.059	.64	155	.080	.90

Background Concentrations:

Low Ozone Case:

$[O_3]$ = .1 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00455 ppm, $[NO_2]$ = .0455 ppm

High Ozone Case:

$[O_3]$ = .2 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00238 ppm, $[NO_2]$ = .0476 ppm

PLANT - WAUKEGAN

STABILITY	WIND SPEED METERS/SEC	DISTANCE OF NO_x PEAK FROM 1ST STACK (m)	NO_x IN EXCESS OF BACKGROUND NO_x (ppm)	LOW OZONE BACKGROUND			HIGH OZONE BACKGROUND		
				NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 / EXCESS NO_x (ppm)	NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 / EXCESS NO_x (ppm)
				$\mu g/m^3$	ppm		$\mu g/m^3$	ppm	
B	1	11600	.093	109	.059	.64	155	.084	.90
B	2	4400	.127	126	.068	.54	206	.112	.88
B	3	3200	.204	134	.073	.36	241	.130	.64
C	3	7200	.105	117	.063	.60	174	.094	.90
C	4.5	5600	.126	126	.068	.54	205	.111	.88
C	6	4400	.139	130	.071	.51	222	.120	.87
D	6	19600	.046	65	.035	.77	78	.042	.93
D	7	16800	.049	69	.037	.76	85	.046	.93
D	8	14800	.053	73	.040	.75	90	.049	.92

Background Concentrations:

Low Ozone Case:

$[O_3]$ = .1 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00455 ppm, $[NO_2]$ = .0455 ppm

High Ozone Case:

$[O_3]$ = .2 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00238 ppm, $[NO_2]$ = .0476 ppm

PLANT - JOLIET

STABILITY	WIND SPEED METERS/SEC	DISTANCE OF NO_x PEAK FROM 1ST STACK (m)	NO_x IN EXCESS OF BACKGROUND NO_x (ppm)	LOW OZONE BACKGROUND			HIGH OZONE BACKGROUND		
				NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 EXCESS NO_x (ppm)	NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 EXCESS NO_x (ppm)
				$\mu g/m^3$	ppm		$\mu g/m^3$	ppm	
B	1	11600	.107	118	.064	.56	177	.096	.90
B	2	4800	.226	144	.078	.35	309	.167	.74
B	3	3200	.276	148	.080	.29	332	.180	.65
C	3	8400	.180	139	.076	.42	271	.147	.82
C	4.5	6000	.219	144	.078	.36	304	.165	.75
C	6	4800	.242	146	.079	.33	318	.172	.71
D	6	23600	.070	91	.049	.71	119	.064	.92
D	7	20000	.077	97	.053	.69	130	.070	.91
D	8	18000	.082	102	.055	.67	139	.075	.91

Background Concentrations:

Low Ozone Case:

$[O_3]$ = .1 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00455 ppm, $[NO_2]$ = .0455 ppm

High Ozone Case:

$[O_3]$ = .2 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00238 ppm, $[NO_2]$ = .0476 ppm

PLANT - FISK

STABILITY	WIND SPEED METERS/SEC	DISTANCE OF NO_x PEAK FROM 1ST STACK (m)	NO_x IN EXCESS OF BACKGROUND NO_x (ppm)	LOW OZONE BACKGROUND			HIGH OZONE BACKGROUND		
				NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 EXCESS NO_x	NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 EXCESS NO_x
				$\mu g/m^3$	ppm	(ppm)	$\mu g/m^3$	ppm	(ppm)
B	1	4000	.128	127	.069	.54	207	.112	.88
B	2	2400	.182	139	.076	.42	273	.148	.81
B	3	2000	.210	143	.077	.37	298	.162	.77
C	3	4000	.157	135	.073	.46	266	.133	.85
C	4.5	2800	.178	139	.075	.42	270	.146	.82
C	6	2400	.187	140	.076	.41	278	.151	.81
D	6	8800	.079	99	.054	.68	133	.072	.91
D	7	8000	.082	101	.055	.67	137	.074	.91
D	8	7200	.083	103	.056	.67	140	.076	.91

Background Concentrations:

Low Ozone Case:

$[O_3]$ = .1 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00455 ppm, $[NO_2]$ = .0455 ppm

High Ozone Case:

$[O_3]$ = .2 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00238 ppm, $[NO_2]$ = .0476 ppm

PLANT - BETHLEHEM STEEL

STABILITY	WIND SPEED METERS/SEC	DISTANCE OF NO_x PEAK FROM 1ST STACK (m)	NO_x IN EXCESS OF BACKGROUND NO_x (ppm)	LOW OZONE BACKGROUND			HIGH OZONE BACKGROUND		
				NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 / EXCESS NO_x (ppm)	NO_2 IN EXCESS OF BACKGROUND NO_2		EXCESS NO_2 / EXCESS NO_x (ppm)
				$\mu g/m^3$	ppm		$\mu g/m^3$	ppm	
B	1	4800	.225	144	.078	.35	308	.167	.74
B	2	2800	.334	151	.082	.24	347	.188	.55
B	3	2000	.421	153	.083	.20	356	.193	.46
C	3	4000	.312	150	.081	.26	342	.185	.59
C	4.5	2800	.381	152	.082	.22	352	.190	.50
C	6	2400	.427	153	.083	.19	356	.193	.45
D	6	8800	.180	139	.075	.41	272	.147	.82
D	7	7600	.196	141	.077	.39	286	.155	.79
D	8	6400	.207	143	.077	.37	296	.152	.77

Background Concentrations:

Low Ozone Case:

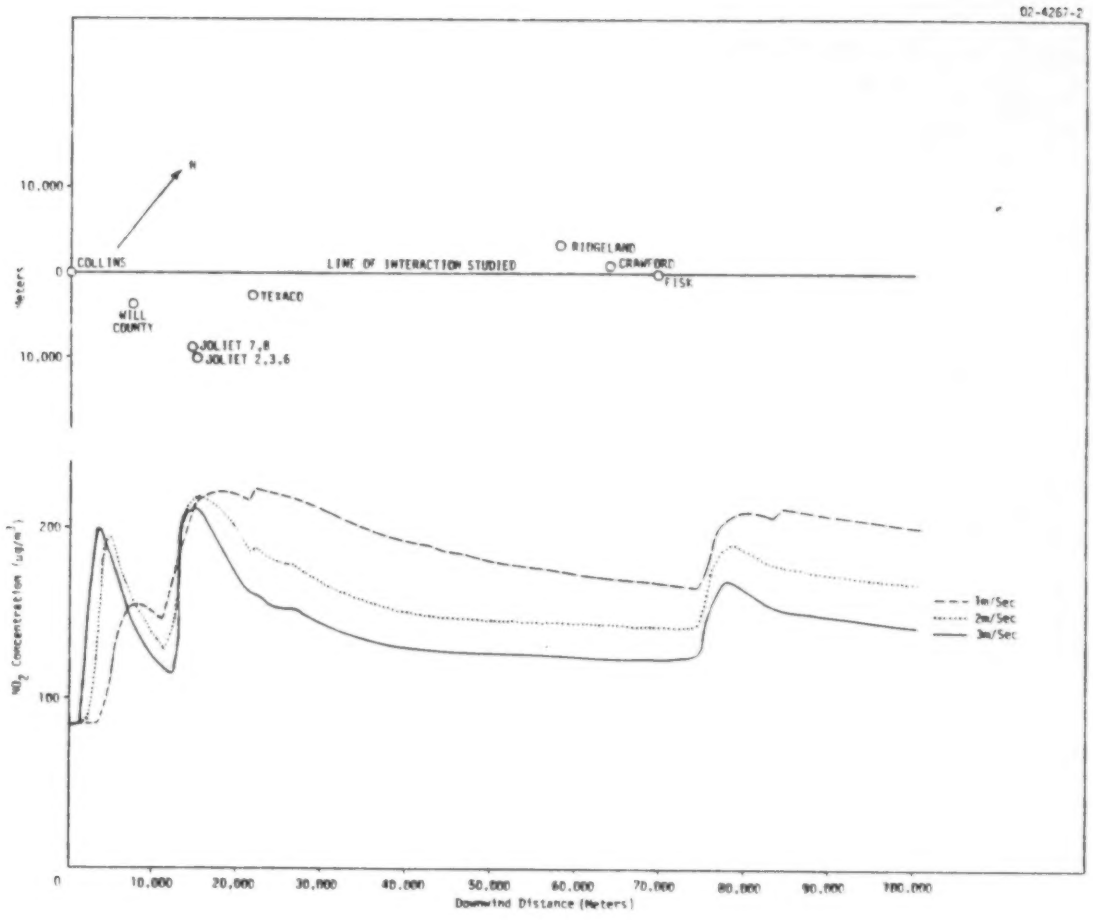
$[O_3]$ = .1 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00455 ppm, $[NO_2]$ = .0455 ppm

High Ozone Case:

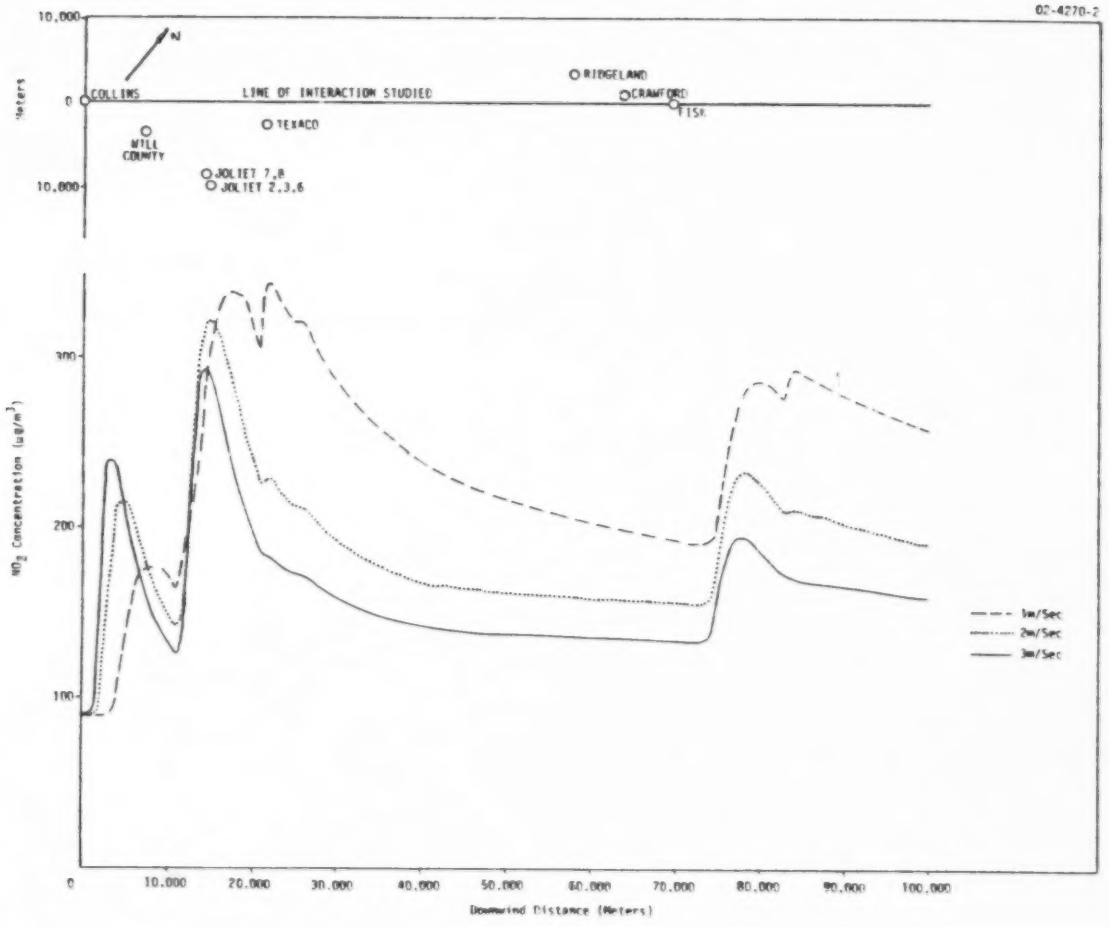
$[O_3]$ = .2 ppm, $[NO_x]$ = .05 ppm, $[NO]$ = .00238 ppm, $[NO_2]$ = .0476 ppm

APPENDIX E

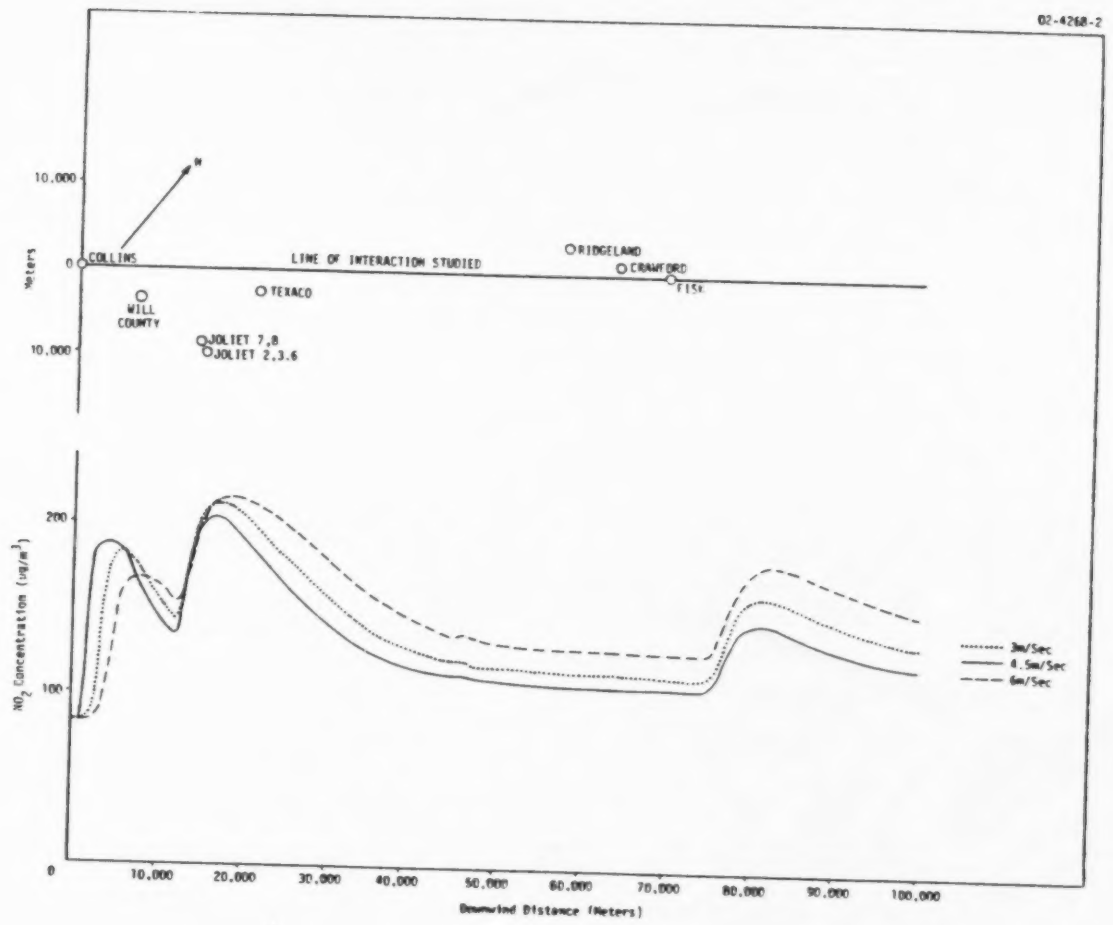
PREDICTED NO_2 CONCENTRATION FOR INTERACTION OF EIGHT CHICAGO-AREA POWER PLANTS--REACTIVE PLUME MODEL



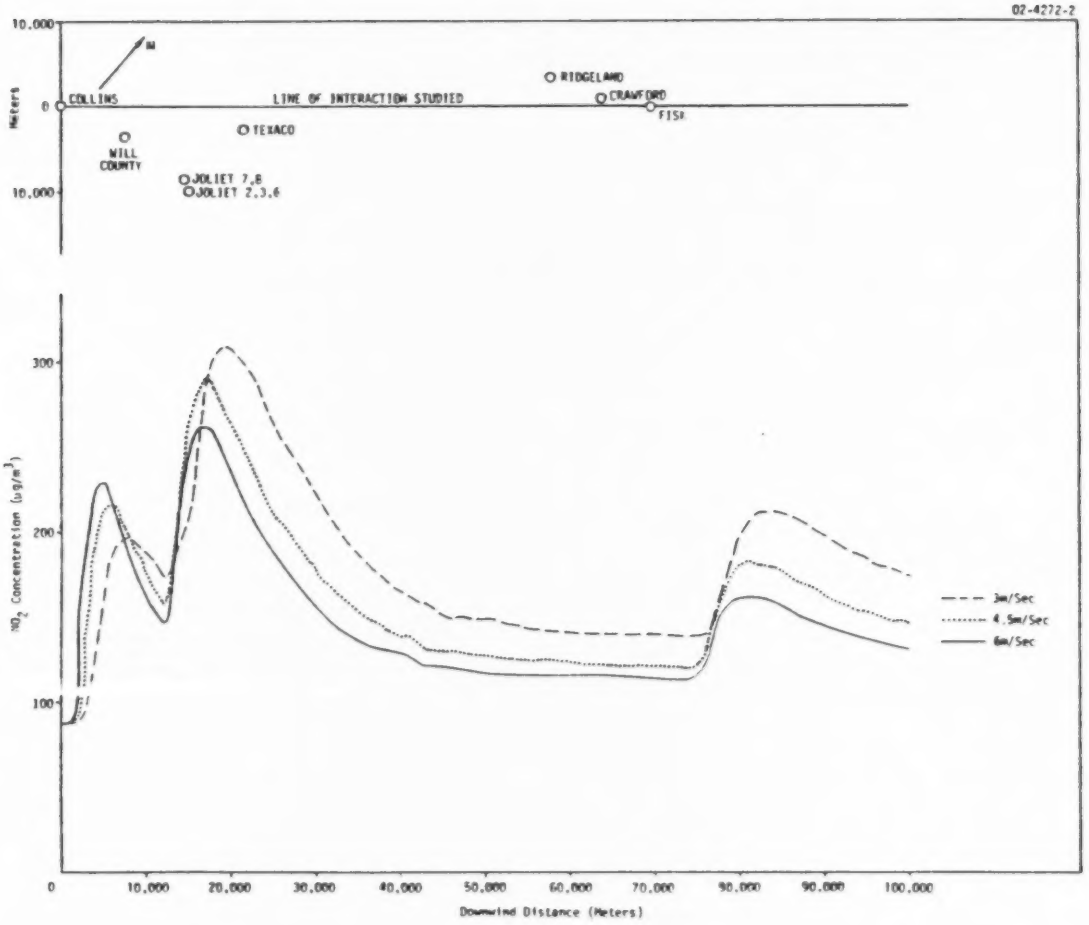
INTERACTION CASE FOR B STABILITY, LOW OZONE



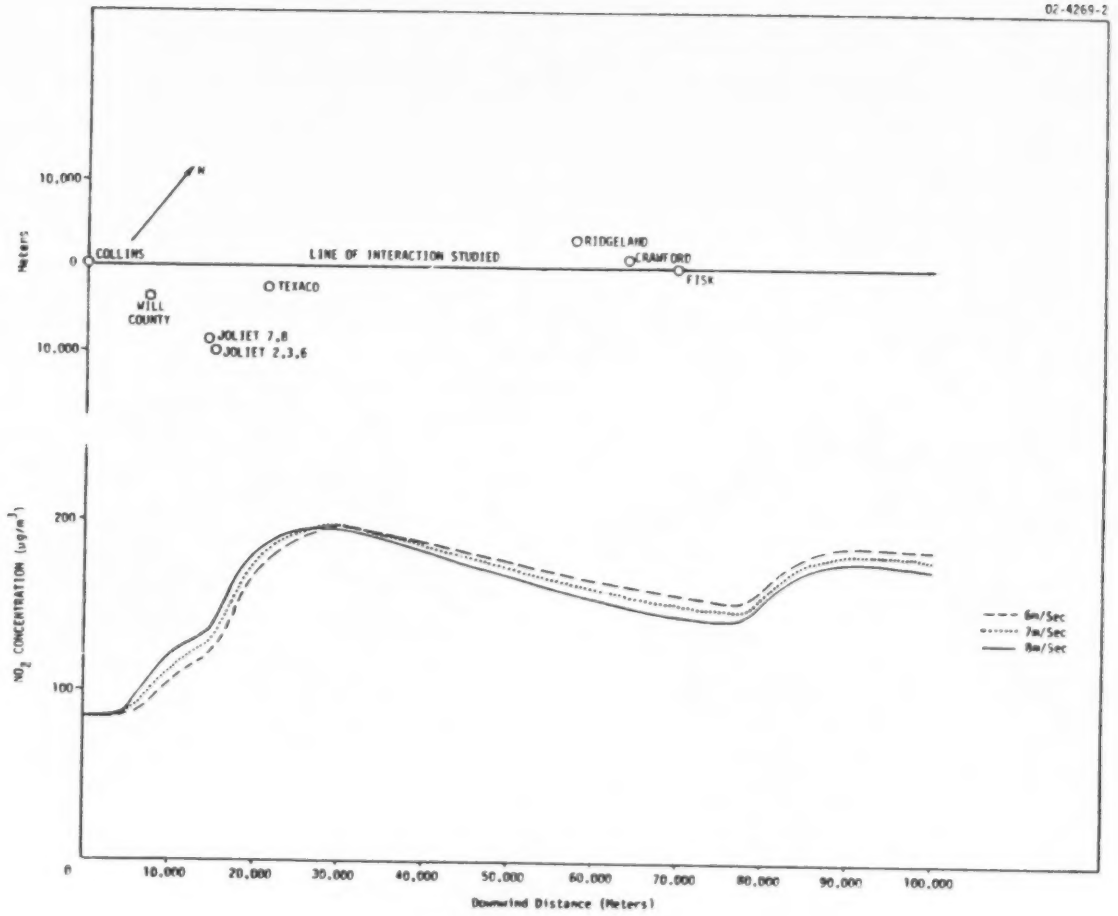
INTERACTION CASE FOR B STABILITY, HIGH OZONE



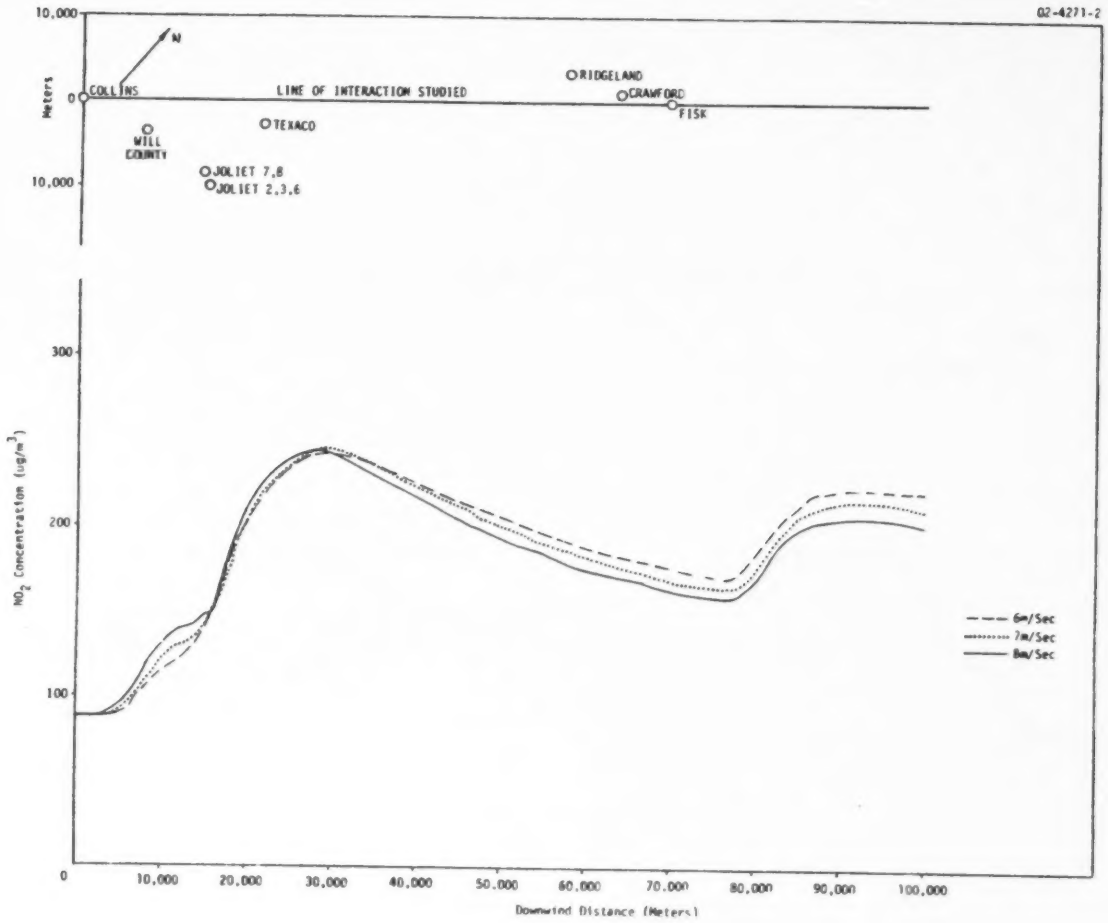
INTERACTION CASE FOR C STABILITY, LOW OZONE



INTERACTION CASE FOR C STABILITY, HIGH OZONE



INTERACTION CASE FOR D STABILITY, LOW OZONE



INTERACTION CASE FOR D STABILITY, HIGH OZONE